NANOCOMPOSITE BARRIER FABRIC FOR CHEMICAL AND BIOLOGICAL AGENT RESISTANT TENT

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ABSTRACT

Different polymer nanocomposites were prepared during this study. The polymer matrix, the nanoclay type and loadings were systematically varied. Processing conditions (screw speed, configuration, and temperature profile) were varied as well in order to find the optimum conditions for nanocomposite synthesis. Dispersion and exfoliation of nanoclays in the polymer nanocomposites were characterized via XRD and TEM. Single and multi layer films were prepared initially in lab scale and characterized. Subsequently, a 62" multilayer blown film was made and laminated into a fabric for tent applications. The liner material was characterized for chemical agent (HD/GB) barrier properties, flame retardant, and mechanical properties. Results showed that the new liner material offers up to 72 hours protection against HD and GB chemical agents. The new tent liner material showed good heat sealability. A full M28 tent liner was manufactured at the end and submitted for further testing. This technology has the potential to realize immediate utilization in currently used tentage systems, as well as long-term feasibility for its transition to future programs, including the Joint Expeditionary Collective Protection (JECP) program.

1. INTRODUCTION

The objective of this work was to develop a new tent liner material for superior defense against chemical and biological agents via incorporating layered nanoparticles into commodity polymers. The new tent liner described here is made of a core ethylene vinyl alcohol (EVOH) nanocomposite sandwiched between two layers of low density polyethylene (LDPE). The core layer of EVOH offers the required barrier properties, while the LDPE layers protect EVOH from humidity. This multilayer film is then laminated into the high density polyethylene (HDPE) fabric to make the tent liner.

Polymer / clay nanocomposites have attracted much attention as researchers attempt to further enhance the properties of polymers beyond what is achievable from more conventional particulate-filled or micro-composites.

Specifically, nanoclays have been widely used as inorganic reinforcements for polymer matrices to create polymer nanocomposites with nanoscale dispersion of the inorganic phase within the polymer matrix.[1-7] These inorganic nanofillers can be readily compounded with thermoplastic resins such as Nylon, PET, polyolefins, or EVOH. The typical feature size of each filler platelet is approximately 1 nm in thickness, and 100-500 nm in length. Owing to their ultrafine feature size, these filler particles do not significantly impact the strength, or the puncture resistance of the base resin. In fact, the material remains highly flexible - a feature of paramount importance in tentage applications. In addition, the high aspect ratio of the layers generates a tortuous path for the diffusing chemical species (Fig. 1), thus significantly increasing the diffusion distance through the thickness of the plastic. The flame-resistance of the material is also enhanced significantly since the nanosilicate layers not only starve the fire, but also keep the structure together by forming an inorganic char layer on the surface.[8] Thus, there is a potential for creating a new generation of cost-effective, extremely high-barrier polymer film material with enhanced chemical and fire-resistance.
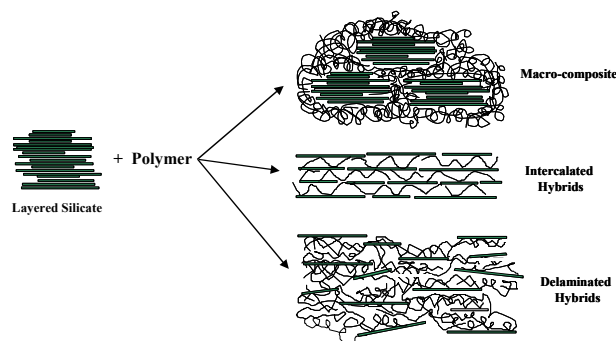
Fig. 1, Schematic of Polymer-Layered Nanoclay Nanocomposite Structures.

However, making true nanocomposites with the nanoclay being homogenously dispersed and fully exfoliated is still a challenge. The design of these nanocomposites involves the creation of favorable interactions at the polymer-layered inorganic interface.

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This is achieved by making the chemistry of the inorganic reinforcement phase more compatible with the organic polymer matrix, i.e., by making the surfaces of the individual layers organophilic. The normally hydrophilic surfaces can be rendered organophilic after ion-exchange reactions of loosely held cations in the interlayer spaces of the inorganic structure with organic cations. The processing conditions of nanocomposites also affect the final structure of composites.

2. MATERIALS

The materials used for this program are Dow LDPE (683I), and Evalca EVOH (E105). The LDPE is a film grade, suitable for both thick and thin film applications. Evalca's E105 has been chosen for it's excellent gas barrier at high humidity, ease of processability and suitability for extrusion coating applications. New chemistries and processing parameters for further improvements were also be investigated and described in the following sections.

3. EVOH NANOCOMPOSITES

To obtain the maximum improvement in polymer performance, it is desirable that the nanoclay particles be homogeneously distributed throughout the polymer on the nanoscale. This distribution is governed by the interactions between the individual clay platelets and the polymer chains. Different chemical modifications and various processing conditions during nanocomposite synthesis were employed to improve the dispersion of clays in the EVOH and its exfoliation.

3.1 Chemical Modification of Clays

Nanoclay modification experiments were designed to decrease the hydrophilicity of the clay surface so that it is compatible with both hydrophilic and hydrophobic components of the EVOH block copolymer. Cloisite® 93A (Southern Clay Products, Gonzales, TX) is montmorillonite modified using a methyldihydrogenated tallow ammonium cation, with the alkyl chain containing primarily 16 to 18 carbon atoms. The effect of the carbon chain length on the hydrophobicity of the alkyl group (hence the polymer clay interaction) was studied. Three new modified nanoclays were synthesized during this study using the following modifying groups: myristyltrimethylammonium cation, $C_{14}H_{29}$ $(CH_3)_3N^+$, tetrahexylammonium cation, $(C_6H_{13})_4N^+$, and tetrapropylammonium cation, $(C_3H_7)_4N^+$.

Modified clays were prepared by contacting a 2.5wt% slurry of a sodium montmorillonite clay with excess of a solution of the bromide salts of the above cations,

assuming a clay cation exchange capacity of 1 meq/g. The mixture was then stirred for 2 hours, filtered and washed with deionized water until the washing tested negative for bromide using silver nitrate solution. The modified clays were then dried, ground and stored prior to use. Analysis of the samples was performed using X-Ray powder diffraction (Fig. 2) and thermogravimetric analysis (TGA). A summary of the data obtained is given in Table 1.
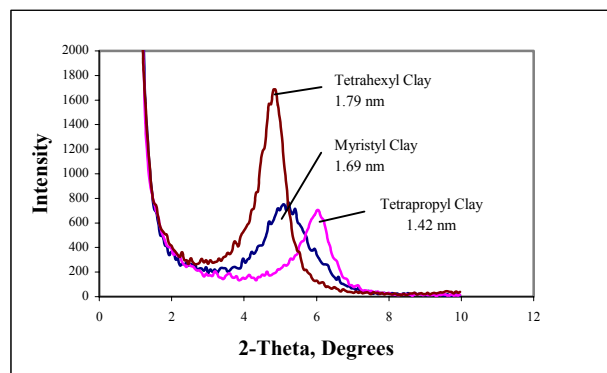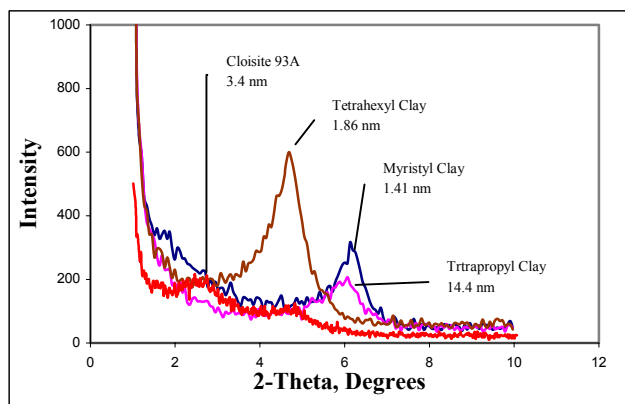

Fig. 2, XRD of modified clays.

Table 1. Characteristics of modified clays

Modifying Cation	Carbon Chain Length	Weight loss (to 900 °C) %	Interlayer Space (Å)
Methyl dihydrogenated tallow ammonium	18	40	23.6
Myristyl Trimethyl ammonium	14	25.2	16.9
Tetrahexyl-ammonium	6	25.8	17.9
Tetrapropyl-ammonium	3	17.6	14.2

The interlayer space of the myristyltrimethylammonium modified clay is lower than would be expected for a C-14 chain, suggesting that the alkyl chain is not oriented perpendicularly between the clay layers, but instead lies at lower angle resulting in a decreased d-space. The hydrophobicity of the clays would be expected to decrease with decreasing chain length.

The three modified clays described above were then compounded with EVOH at a 5% loading. These experiments were conducted in a Brabender Plasticorder (Model DR-2071). Samples were analyzed via XRD and TEM to evaluate changes in the dispersion and distribution of the nanoplatelets through the polymer matrix.

XRD of the nanocomposites (Fig. 3) showed similar peaks with the ones observed in the XRD of modified nanoclays alone, which suggest that at least part of the clays has not interacted with polymer. This can be due to poor dispersion of the clays or lack of strong interactions between the nanoclay surface and the EVOH. TEM data indicated a minor or no improvement on dispersion of all three nanoclays in the EVOH, which is in agreement with the XRD data. In other words, the degree of dispersion and exfoliation did not seem to improve with these chemical modifications. In fact, the XRD of the nanocomposite with Cloisite® 93A suggest that this nanoclay is dispersed better than our modified nanoclays. Therefore it was decided to pursue with the commercially available clay, Cloisite® 93A, for further experiments.

Fig. 3, XRD of EVOH nanocomposites with modified clays.

3.2 Processing Conditions

In addition to chemical modifications, variations of processing conditions were also applied with intention of improving the dispersion of the clays into the polymer system. Three different screw configurations, two different screw speeds, and two different temperature profiles were used in this study. Although it was not possible to achieve nanoscale uniform dispersion and full exfoliation of the nanoclay into EVOH, it was noted that varying the processing conditions influenced the dispersion of nanoclay particles. The TEM pictures showed areas with well dispersed and well exfoliated clays along side with relatively large clay agglomerates (see Fig. 4).

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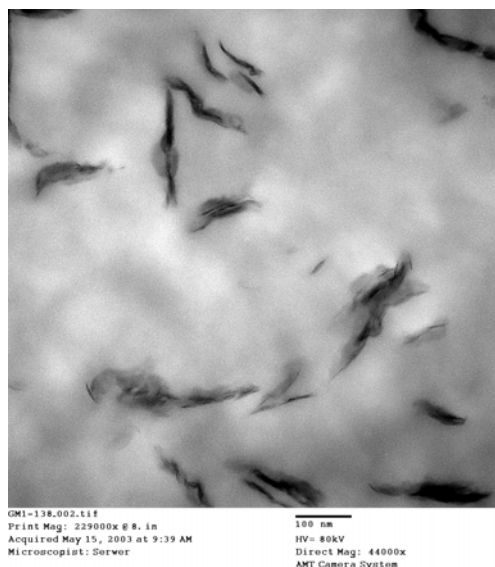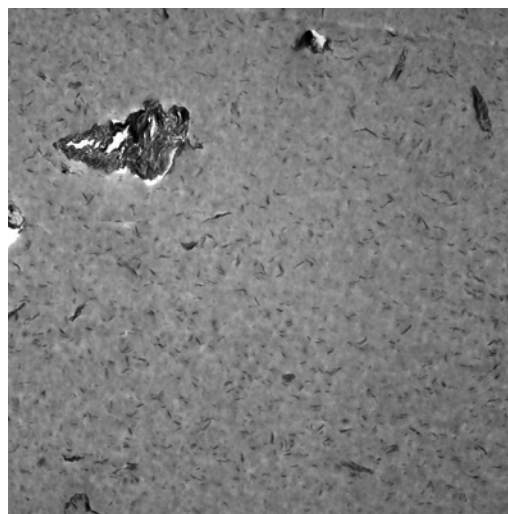
**Fig. 4, Representative TEM micrographs of 5% Cloisite® 93A in EVOH nanocomposites.**

4. MULTILAYER FILM AND TEST RESULTS

The EVOH nanocomposite containing 5% of Cloisite® 93A clay in it was used to make the multilayer barrier film. First the three layer blown film was made (EVOH nanocomposite core sandwiched between two layers of LDPE). A thin layer of a maleated LDPE (Polybond 3109) was used as a tie layer between the EVOH and LDPE. The thickness of the EVOH layers and the overall film is given in Table 2.

Table 2. Target film properties for multilayer blown film

| Thickness of film overall	Thickness of EVOH Layer
4.00 mil	1 mil
3.45 mil	0.5 mil
3.20 mil	0.25 mil

This film was then laminated to the Fabrene HDPE scrim. The resulting tent liner was tested for mechanical properties as shown in Fig. 5 - Fig. 8. From these figures it was concluded that the addition of nanoparticles in the EVOH layer generally improved the mechanical properties studied here. Addition of the nanoparticles was found to have the greatest effect on the film stiffness as expected and an up to 150% improvement in tensile modulus was observed. Similarly, the presence of the nanoparticles in the EVOH layer leads to increases in tear propagation. It was however surprising that the increase was more pronounced in films with a thinner EVOH layer.
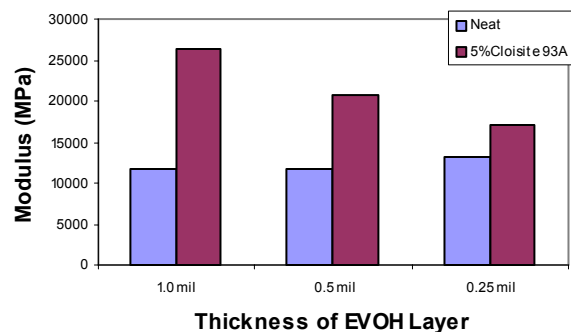
**Fig. 5, Effect of Thickness of EVOH Layer on Modulus.**
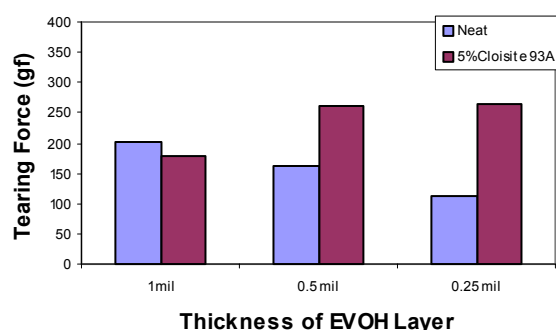
Fig. 6, Effect of Film Thickness on Tear Propagation (Machine Direction).
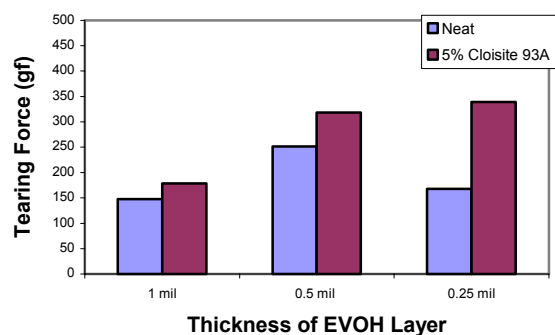
Fig. 7, Effect of Film Thickness on Tear Propagation (Transverse Direction).

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Table 3. Chemical Agent Permeation Results

| Agent | Sample | Sampling Intervals (Hours from Start) | | | | | | | | |
		(0-2)	(2-4)	(4-6)	(6-8)	(8-12)	(12-24)	(24-48)	(48-72)	Cumulative
HD	Neat	ND	ND	ND	ND	ND	ND	0.1	0.15	0.25
	5% nano	ND	ND	ND	ND	ND	ND	ND	0.2	0.2
GB	Neat	ND	ND	ND	ND	ND	0.00016	0.00036	0.00037	.00089
	5% nano	ND	ND	ND	ND	ND	ND	ND	ND	ND
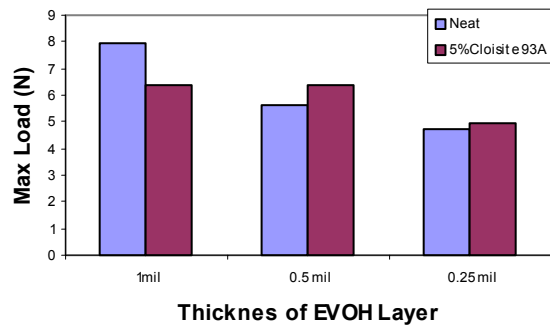
Fig. 8, Tear Initiation Test Results.

4.1 Chemical Agent Resistance

Table 3 displays the results of the tests conducted at GeoMet Labs. The data below shows that Triton's nanocomposite barrier film passes 48 hours exposure to HD chemical agent with no breakthrough and 72 hours with no detectable amount of GB agent breakthrough. It can be seen that the film with the nanocomposite EVOH layer in it had some improvements on the chemical barrier over the film with neat EVOH, suggesting that the presence of the nanoclay in the EVOH improved the barrier properties of the multilayer film.

The chemical agent protection of liner materials is usually evaluated via chemical permeation/breakthrough test. During this program, all materials were first tested with simulant, and then the best candidates were selected and the final product were tested with real chemical agent at GeoMet Laboratories.

GeoMet Laboratories tested samples of the multi-layer barrier film for a period of 72 hour against GB and HD chemical agents. PTFE was which shows no agent breakthrough over a 72-hour testing period used as a control.

5. TENT LINER MANUFACTURING AND TESTING

Finally, a full size M28 tent liner was manufactured based on multiplayer barrier film described above. The mechanical and chemical barrier testing showed that this liner meets or exceeds the requirements for the CB protective liner. The mechanical properties of the tent liner that is relevant to field application is shown in Table 4.

Table 4. Mechanical Properties of Prototype tent liner

Property		Initial	After Weathering
Burst Strength (Grab), lb	Warp	166.6 (±12)	168.1 (±5.7)
	Filling	190.8 (±3.3)	177.5 (±14.5)
Break Elongation (Grab), %	Warp	15.4 (±1.2)	16.3 (±0.6)
	Filling	15.2 (±0.3)	14.7 (±0.8)
Tear Strength (Tongue), lb	Warp	17.8 (±1.3)	13.6 (±3)
	Filling	12.7 (±4.3)	17.9 (±2.7)
Ply Adhesion	-	2.8	6.1

6. NANOCOMPOSITE FOR FLAME RETARDANT APPLICATIONS

Unlike active flame retardant additives that are used to prevent ignition of the polymer, layered silicates (nanoclays) are referred to as passive flame retardants. In a polymer nanocomposite, the layered nanoclays act as a barrier to flame propagation and heat evolution by the formation of a ceramic or glassy layer on the surface of the polymer.

Several LDPE nanocomposite materials were fabricated to evaluate the flammability and processability of LDPE filled with both Triton's nanoclay as well as commercially available flame-retardants. In these

experiments, a combination of active flame retardants (FlameStab and Cyagard) and nanoclays were used to evaluate any synergistic effect on suppressing the flammability of the polymer.

Each of these materials were molded into plaques (6"x4"x1/8") and cut into test specimens (5"x1/2"x1/8"). The flammability properties were tested according to UL 94 vertical burn testing procedures. The data for the time to ignition and polymer drip are shown in Fig. 9 and Fig. 10.

Observations:
1. Time to ignition is generally improved with the incorporation of nanosilicates
2. Time to drip has been dramatically improved with the incorporation of nanosilicates
3. The flame retardants have a positive effect on the time to ignition
4. The flame retardants improve the time to polymer drip, but this improvement is insignificant compared to the effect of the nanosilicates

The next step would be to use LDPE nanocomposite for barrier film and evaluate for tentage applications.
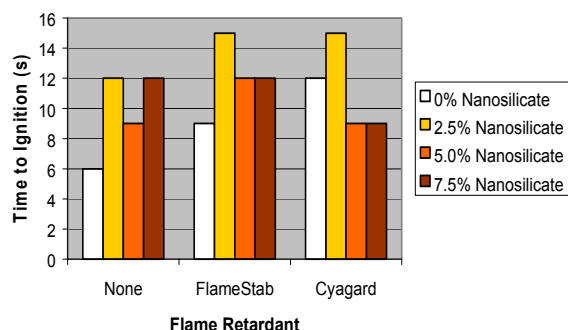
Fig. 9, Time to ignition for LDPE with nanosilicates and flame retardants.
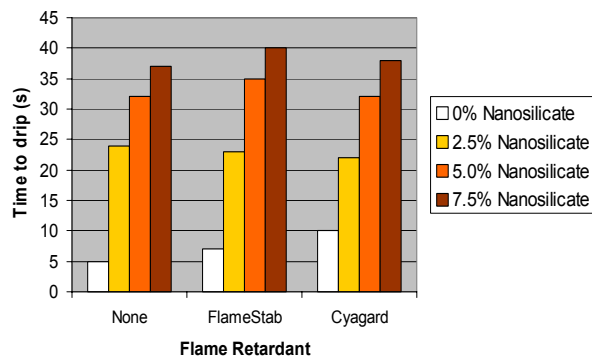
Fig. 10, Time to Polymer Drip for LDPE with Nanosilicates and Flame Retardants.

7.   CONCLUSIONS

EVOH nanocomposites were successfully fabricated via melt extrusion of commercial Cloisite 93A with EVOH. Although perfect exfoliation was not achieved, mixed morphology of individual exfoliated nanoclay particles with intercalated aggregates was confirmed using XRD and TEM. This material was used to fabricated a new tent liner material consisting of a nanoclay filled EVOH inner layer sandwiched between two LDPE layers. A prototype tent was made using this film and successfully tested for mechanical and chemical barrier properties. The tent liner material showed >72 hours protection to GB and >48 hour protection to HD which meet the US Army requirements for JECP. Addition of nanoclay in the EVOH layer also showed improvements in tensile modulus of the film and resisted tear initiation and tear propagation compared with multilayer films with neat EVOH. Additionally, it was demonstrated the applicability of dispersed nanoclay layers in LDPE as an effective flame retardant.

The results so far point towards the feasibility of using this approach to develop a new tent liner material as a promising candidate to improve the flame and barrier properties above the current M28 liner and meet the goals of the JECP program.

REFERENCES

[1] Giannelis, E. P., 1996: *Advanced Materials*, **8,** 29.
[2] Vaia R. A., Ishii H. and Giannelis E. P., 1995: *Chem. Mater*., **5,** 1694.
[3] Burnside S. D. and Giannelis E. P., 1995: *Chem. Mater*., **7,** 1597.
[4] Kojima Y., Usuki A., Kawasumi M., Okada A., Fukushima Y., Kurauchi T. and Kamigaito O., 1993: *J. Mater. Research*, **8,** 1185.
[5] Messersmith P. B. and Giannelis E. P., 1993: *J. Polymer Sci., Part A*, **33,** 1047.
[6] Yano K., Usuki A., Okada A., Kurauchi T. and Kamigaito O., 1993: *J. Polymer Sci., Part A*, **31**, 2493.
[7] Lan T. and Pinnavaia T. J., 1994: *Chem. Mater.*, **6**, 2216.
[8] Gilman J. W., Kashiwagi T. and Lichtenhan J.D., 1997: *SAMPE Journal*, **33,** 40.